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Self-organized monolayer of *meso*-tetradodecylporphyrin coordinated to Au(111)

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Preparation of Monolayers on Au(111). The gold on mica substrates were prepared by evaporation of 99.99% gold, Umicore Materials AG, on freshly cleaved mica sheets, Ted Paella, Inc., at 10^{-7} mbar in a home-built evaporator in the Materials Science Centre, University of Groningen. The thickness of the gold layer was ~150 nm. A test sample was employed in every case to check for reconstruction of the Au(111) surface by using STM in air or in *n*-tetradecane. Prior to STM imaging, H_2P was dissolved in *n*-tetradecane (Aldrich) at a concentration of 0.1 mM by sonication (~5 min) and heating at ~40^o (~1h). A drop of the purple solution of H_2P was applied to a freshly prepared Au(111) surface and the STM tip immersed into the solution.

Preparation of Monolayers on HOPG. Prior to imaging, the porphyrins were dissolved in *n*-tetradecane (Aldrich) at a concentration of 0.1 mM by sonication (~5 min) and heating at ~40^o (~1h). A drop of the solution was applied to a freshly cleaved surface of HOPG (Goodfellow) and the STM tip immersed into the solution.

Scanning Tunneling Microscopy (STM). All experiments were performed at room temperature, using a PicoSPM (Scientec). Pt/Ir STM tips were prepared mechanically from Pt/Ir wire (80:20, diameter 0.25 mm, Goodfellow). The parameters of the unit cells were measured after drift effects were

corrected with the Scanning Probe Image Processor (SPIP) software (Image Metrology ApS). However, the presented STM images contain raw data and are not subjected to any processing other than routine plane correction.

Determination of orientation of H_2P monolayer on HOPG. Imaging HOPG beneath the molecules allows for the determination of the orientation of the physisorbed molecules with respect to the main crystallographic axes of the HOPG surface. The imaging of the underneath substrate can be done either by increasing the setpoint intensity or by decreasing the tunnelling voltage, which brings the tip closer to the surface.[1] In the case of the STM image shown in Figure S1, different features were obtained first by increasing set-point during bottom up scanning (V_T = -0.374 V), from i_T= 11 pA (bottom part) to 39 pA (middle section). Then the voltage was changed to a positive value (V_T= 0.379 V) keeping the set-point constant (i_T = 39 pA).

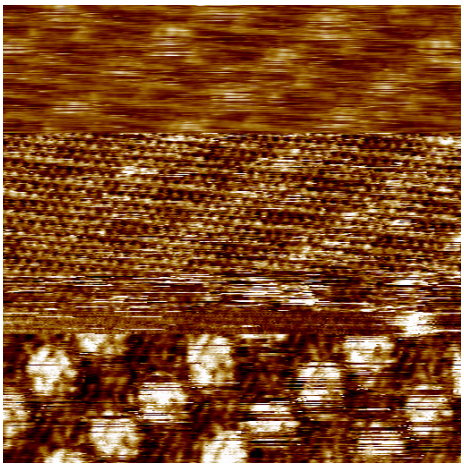

Figure S1 STM image (10.2 nm x 10.2 nm). Imaging the HOPG surface beneath the molecules allows for the determination of the orientation of the physisorbed alkyl chains with respect to the main axes of the HOPG surface.

X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were performed with an X-probe Surface Science Laboratories photoelectron spectrometer equipped with an Al Kα monochromatic X-ray source (hν=1486.6 eV). The overall energy resolution was set to 1.0 eV and the photoelectron take-off angle was 37°. The binding energies were referenced to the Au $4f_{7/2}$ core level. The base pressure in the spectrometer was in the low 10^{-10} Torr range. Photoemission spectra of the C 1s, N 1s, Au 4f regions were measured for each point of the sample. A minimum number of scans were accumulated on each point to avoid X-ray induced damage.

Spectral analysis included a linear background substraction for N 1s. A Shirley background could not be applied to the N1s signal of the monolayer spectrum because the N 1s line is affected by the secondary electron background of the Au 4d signal. Peak separation was achieved by using mixed Gaussian-Lorentzian functions in a least-squares curve-fitting programm (Winspec) developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. The procedure consisted of fitting the minimum number of peaks that can reproduce the spectral data and are consistent with the molecular structure of the film.

Synthesis. H_2P was synthesized by a modified literature procedure (Scheme 2).[2] A mixture of 200 mL of nitrobenzene and 125 mL of AcOH was heated to 120 ºC in air. Tridecanal (5.0 g, 25 mmol) and pyrrole (1.75 mL, 25 mmol) were then added and the reaction mixture stirred at 120 ºC for 1 h. The nitrobenzene and AcOH were removed by distillation under reduced pressure and the residue was precipitated from EtOH. The resulting dark solid was purified three times by column chromatography (neutral Al_2O_3, CH_2Cl_2) to afford a dark purple solid which was further purified by precipitation from EtOH to afford 151 mg (2.4 %) of H_2P. ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.62 (s, 2H, 2NH), 0.87 (t, $^3J_{HH}$ = 6.9 Hz, 12H, 4 CH_3), 1.25 – 1.28 (m, 48H, 24 CH_2), 1.49 – 1.56 (m, 16H, 8 CH_2), 1.81 (m, 8H, 4 CH_2), 2.51 (m, 8H, 4 CH_2), 4.93 (t, $^3J_{HH}$ = 8.1 Hz, 8H, 4 CH_2), 9.46 (s, 8H, 8 CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (4 CH_3), 22.7 (4 CH_2), 29.4 (4 CH_2), 29.7 (12 CH_2), 29.8 (4 CH_2), 30.6 (4 CH_2), 40.0 (4 CH_2), 35.5 (4 CH_2), 38.7 (4 CH_2), 118.3 (8 CH), 128.4 (broad s, 8 C), m/z (CI, %) = 983.9 (M^++1, 100).

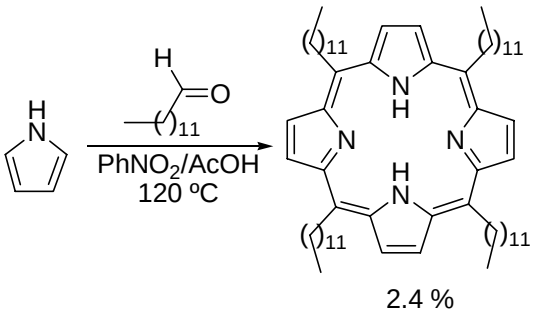

Figure S2 Synthesis of H_2P.

(1) See for example Puigmartı-Luis, J.; Minoia, A.; Uji-i, H.; Rovira, C.; Cornil, J.; De Feyter, S; Lazzaroni, R.; Amabilino, D. B. *J. Am. Chem. Soc*. **2006**, ASAP, DOI 10.1021/ja0640288.

(2) Johnstone, R. A. W.; Nunes, M. L. P. G.; Pereira, M. M.; Gonsalves, A. M. D. R.; Serra, A. C.; *Heterocycles* **1996**, *43*, 1423-1437.

^{1}H and ^{13}C NMR figures: